

Optical Absorption Modeling of Arbitrary Shaped Nanoparticles

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ABSTRACT

Limitations of a method for modeling the optical absorption spectra of nanosize particles is explored. Computer software has been developed to predict absorption peaks based on the particle's geometry. The software breaks the particle's surface into small sites and builds a matrix describing site to site surface polarization interactions. From this matrix the particle's normal mode resonances are determined.

With the method it is possible to simulate nearly any geometrical shape. Cubes with cut corners or edges, such as chemically fabricated silver particles are possible. Long, thin bars are also candidates for simulation. Results dependence on surface resolution is explained.

Keywords: absorption, spectra, simulation, nanoparticle

1 INTRODUCTION

Mie theory and other models have shown good accuracy in predicting the optical response in fields of spherical nanoparticles. These methods are however severely limited in their application to some laboratory experiments. Real particles, of silver or MgO for example, are far from spherical. They are typically cubes or many times cubes with the corners severed. In the case of our current experiments the particle fields may even include rods many times longer than the average cube edge. What is desired is a method of predicting response to particles of any arbitrary shape.

An analytic computer model to predict the absorption portion of optical response in fields of nanoparticles is investigated. In the results presented here particles are assumed to be nanosized cubes. However the method is applicable to nearly any continuous shape without holes. Particles are also assumed to be significantly smaller than the wavelength of incident light. The model considers a single particle and its interaction with incident light,

particle to particle interaction is not modeled. Therefore simulation of experiments with fields of particles is limited to low density, widely spaced particles. The method focuses on surface polarization resonant modes set up with the incident light. These resonant modes are a function of the incident light wavelength, particle geometry and material. The model treats the cube surface as an array of small discrete surface patches with properties similar to the bulk material.

A key assumption is that only surface polarization resonant modes are required to account for complete optical absorption spectra. R. Fuchs [1] has shown that this assumption is valid by correlating calculated results with experiment. Fuchs used the method to predict absorption in fields of cubic MgO and NaCl particles.

2 PATCH MODEL

Only surface mode polarization is considered in the model. Transverse and longitudinal modes are assumed to be insignificant. Conceptually an electric field, \vec{E}_0 is applied to the particle. With \vec{r} just inside the surface polarization is related to susceptibility of the base material by:

$$P(\vec{r}) = \chi(\omega) \vec{E}(\vec{r}) \quad (1)$$

And, where \hat{n} is the normal at the surface it follows that polarization at one point is effected by the entire surface and the incident \vec{E}_0 field. Polarization inside the particle is assumed to be zero.

$$\frac{p(\vec{r})}{\chi(\omega)} = -2\pi p(\vec{r}) + \int_S \frac{\hat{n}(\vec{r}) \bullet (\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} p(\vec{r}') dS' + \vec{E}^0 \bullet \hat{n}(\vec{r}) \quad (2)$$

The first term on the right side of Eq. (2) is a solid angle approximation to account for the polarization at the site of \vec{r} on the surface.

And in discrete form with the surface divided into i equal area patches:

$$[\chi^{-1}(\omega) + 2\pi]p_i = \sum R_{ij}p_j + \vec{E}^0 \cdot \hat{n}_i \quad (3)$$

The polarization at each patch is p_i . R_{ij} is representative of each patch's interaction with each other patch individually. It is a two dimensional matrix where both indices ranges are the total number of patches on the particle. Therefore R_{ij} contains the particle's geometry dependant information. R_{ij} is used in the model to determine resonant peak locations and magnitudes.

$$R_{ij} = \frac{\hat{n}_i \cdot (\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|^3} \Delta S_j \quad (4)$$

Obviously because of the denominator the diagonal elements of R_{ij} must be set equal to zero. The local effect of a patch is represented by the 2π term in Eq. (3).

The polarization Eq. (3) includes the particle geometry in R_{ij} , the material properties in the frequency dependent susceptibility and the local patch approximation. Given a susceptibility value for a specific material Eq. (3) generates a system of equations with one equation and one variable for each patch. Solving the system of equations yields polarization for the entire surface.

Determining if the particular polarization pattern is a significant resonant mode requires calculating the expectation value for the complete particle.

$$\langle \chi \rangle = \frac{|\vec{M}|}{v|\vec{E}_0|} \quad (5)$$

With a uni-directional \vec{E}_0 field the total resultant induced dipole moment, \vec{M} , is related to the average susceptibility by Eq. (5). In Eq. (5) v is simply the volume of the particle.

The total dipole moment may be determined by summing over the polarization at each surface patch.

$$M_1 = \sum_i p_i x_{1i} s_i \quad (6)$$

Where M_1 is the induced dipole moment along one axis direction and x_{1i} is the component of \vec{r} parallel to that axis.

Significant absorption peaks will be characterized by spikes in the imaginary part of the total particle susceptibility expectation value. To find resonant modes the real part of $\chi(\omega)$ is varied from 0 to -1 in small steps. At each step Eq. (3) is solved for the complete surface polarization. The dipole moment and total expectation value of susceptibility are calculated. Peaks indicate at what values of $\chi(\omega)$ resonant modes occur. In general the wider the peak the more significant the resonant mode.

An example of the susceptibility spectrum is shown below in Fig. 1.

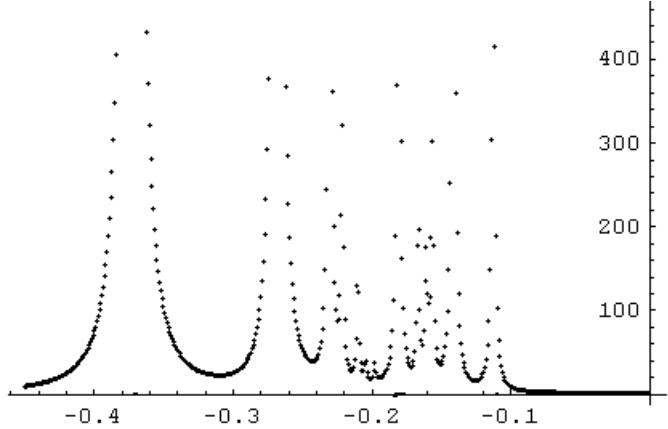


Figure 1: Susceptibility Peaks of a Cube

3 RESOLUTION DEPENDENCE

Of particular interest is the models dependence on the size of each patch (or overall resolution of the surface). As the resolution is increased computer processing time increases exponentially so there are practical limits to the total number of patches.

Figs. 2-5 show normalized resonant peak distributions for a simple cube. Various patch resolutions are shown to illustrate changes in the resultant peaks. Fig. 2, with only 9 patches per cube side was generated in just a few minutes of computer time. Note the low frequency peak that does not show up in higher resolution calculations. This low frequency peak is diminished in Fig. 3 with 16 patches per face. The peak is probably a resonant mode reacting with the patch structure as opposed to the geometry of the cube shape.

Peaks show closer grouping in Fig. 4 with 25 patches per side. Fig. 4 took about one hour to fully process. Finally Fig. 5 ran almost four hours without yielding results greatly different from Fig. 4. For a simple cube 36 patches per side appears to be adequate. However, as more complex geometries are simulated higher resolutions may be required. For example, a cube with cut corners will need to be simulated with patch size small enough to accurately represent the cut face.

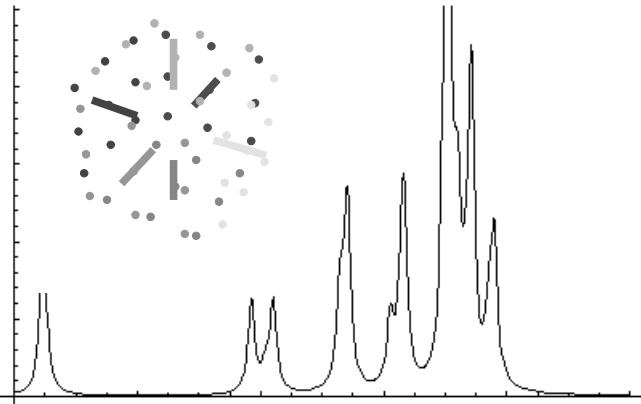


Figure 2: 9 Patches per side

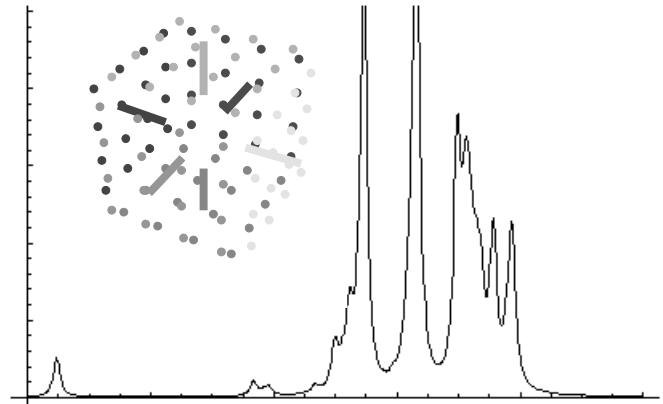


Figure 3: 16 Patches per side

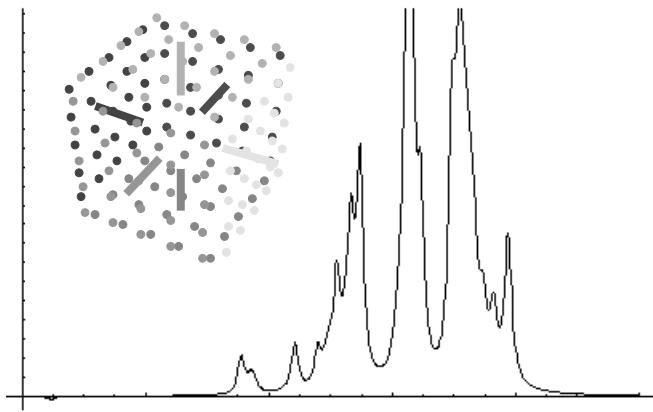


Figure 4: 25 Patches per side

(Processing times are approximate running Mathematica on a Pentium 4 desktop computer)

4 POLARIZATION MODES

As explained in section 2 each absorption peak is associated with a particular resonant mode surface polarization. Once the peaks are found graphics representing the polarization can be generated.

Fig. 5 shows one cube face for the eight most prominent resonant modes. The widest peak results from the mode labeled A to the smaller H. The spectrum for a cube shows about 10 peaks total, two are small enough to be ignored. The first two peaks represent the majority of the response. The spike associated with A is twice the size of B and B in turn is twice the size of C.

5 SOFTWARE

The software model has been developed in Mathematica version 4.2. The first section of the worksheet is dedicated to definition of the particle. The

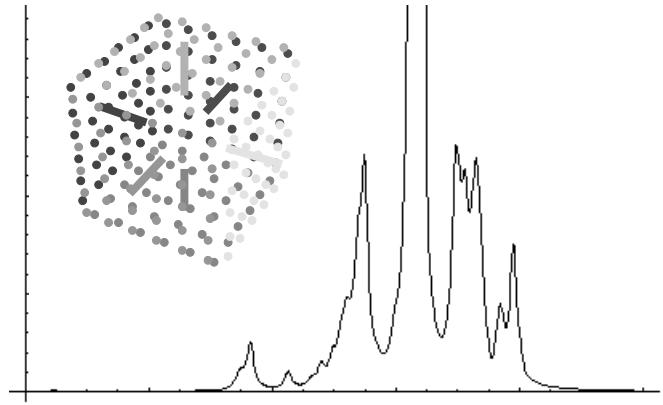


Figure 5: 36 Patches per side

shape is defined by first entering an X, Y, and Z length and a patch resolution. A cube (that can be rectangular) is generated by the program. More complex shapes are achieved by defining planes to cut the cube. An unlimited number of planes may be defined by inputting a normal vector and a point on the plane. The cube is cut with the part in the positive vector direction being discarded. In this fashion cubes with corners or edges cut off can easily be input. Diamond, parallelogram and other shapes are also possible. The program outputs a graphic of the shape, as seen in Figs. 2-5 for verification.

Once the shape is input the program handles all calculations. The large matrix R_{ij} is generated first. The X, Y, and Z coordinates of each patch are recorded in another matrix for reference later.

A range and step size can then be defined for generating the graph of total particle susceptibility. The program loops through solving Eq. (3) for each step in material susceptibility.

Peaks are then picked out by hand and polarization plot like those in Fig. 6 may be generated.

The plots in Figs. 2-5 are generated by applying a realistic material susceptibility. The susceptibility data can be calculated from the standard single oscillator expression or taken from published experimental data such as [3].

REFERENCES

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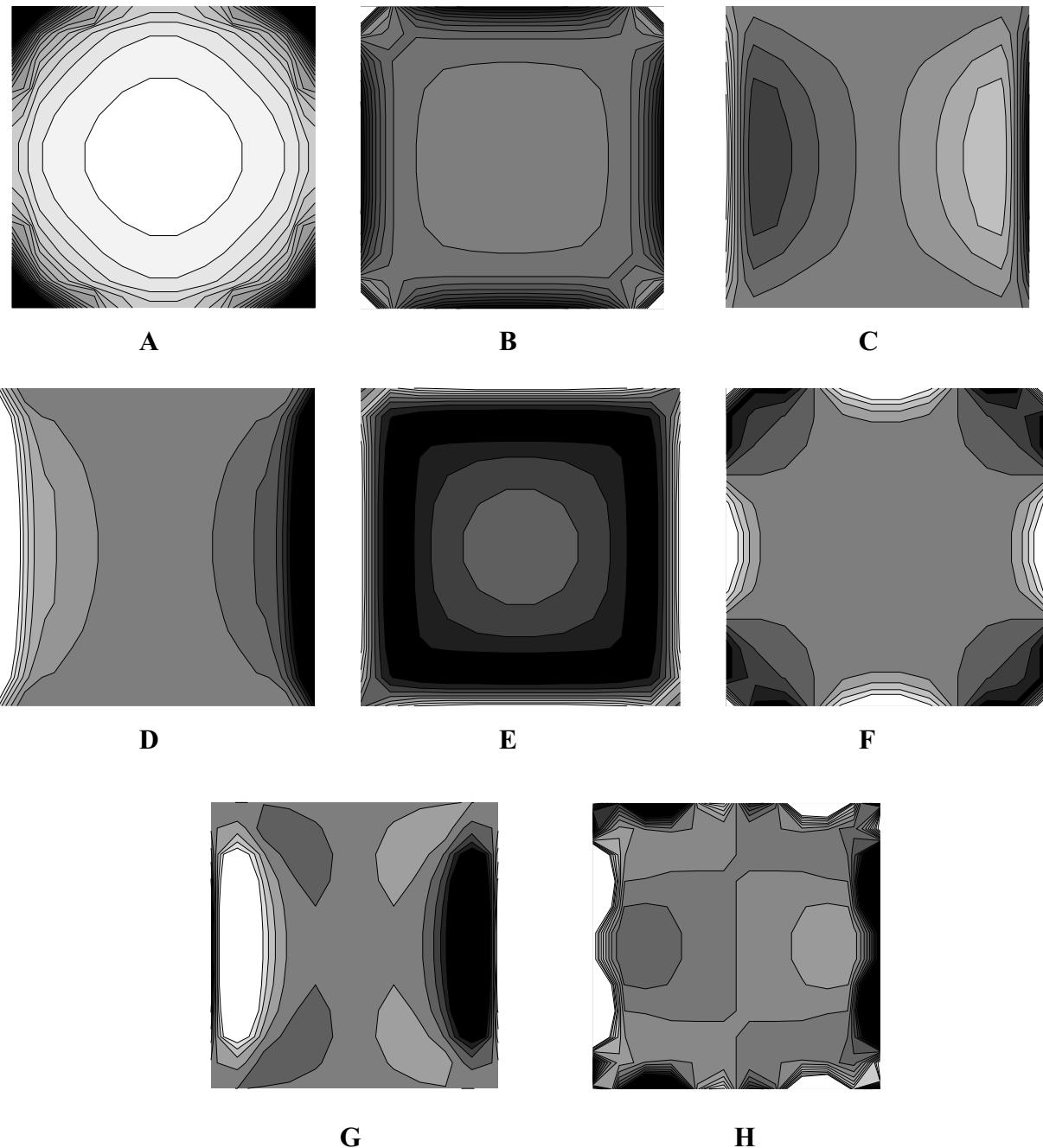


Figure 6: Surface Polarization Patterns for the Eight Most Significant Cube Resonant Modes